Improved deresination during oxygen delignification.
Part II: effects of blended surfactant addition

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Abstract: Washing after the oxygen delignification stage in aspen kraft pulping has been shown to reduce the extractives in pulp. It was previously shown that this can be enhanced by the addition to oxygen delignification of a certain generic surfactant. Further work has now been carried out to investigate the effect of a selection of commercially available surfactant blends on deresination. One of the formulations was particularly effective in enhancing extractives removal in an oxygen stage environment.

Leveraging the extractives continues to be an elusive goal for kraft pulp manufacturers using aspen, birch, or certain tropical hardwoods. Oxygen delignification, followed by washing, typically lowers the extractives of aspen kraft pulp by about 40% [1]. Most of this is attributable to the washing, as very little change occurs to the extractives during the oxygen delignification in the tower itself [2-4]. In 2003, Bouchard et al. [1] found that a linear alcohol ethoxylate (LAE) decreased the extractives by an additional 11% during oxygen delignification and subsequent washing. At the same time, a block copolymer of ethylene oxide and propylene oxide (EO/PO, often referred to as a pluronic) was ineffective at increasing deresination. Hence, not all surfactants are effective, but LAEs show promise.

The results of this earlier work are summarized in Fig. 1, where the dichloromethane (DCM) extractives of pulps, before and after oxygen delignification plus washing, have been plotted. The left two bars show results before and after oxygen delignification, without surfactants, followed by washing. The reduction in extractives is 41%. The third bar shows the extractives content of pulp after oxygen delignification in the presence of a pluronic, at 4 kg/t. It is evident that this surfactant was ineffective at improving deresination between oxygen delignification. The fourth bar shows the effect of adding 4 kg/t linear alcohol ethoxylate. It is evident that, with the LAE, there was a 52% reduction in extractives. This represents an 11% improvement in the percent reduction of DCM extractives versus the blank, with no surfactant.

Since this work, we have looked into the possibility of finding a surfactant blend that is even more effective than a single LAE. Most pitch dispersants used in the pulp and paper industry are blends of surfactants, as there is often synergy, or improved performance, with such blends.

The objective of the work described in the present paper was to explore the use of several blended products containing LAEs for improved deresination in oxygen delignification followed by washing.

EXPERIMENTAL

Pulp

The aspen kraft pulp was from the same mill as the pulp used in Reference 1. Sampled at the stem pipe off the pressure washer prior to the oxygen mixer, it was washed in several dilutions in the laboratory until the pH reached 9.8, to prevent alkaline leaching during storage. The washed pulp was then centrifuged to 33% consistency, fluffed, and stored in a cold room at 4°C. Typical physical properties of unbleached pulps produced at this mill are given in Reference 1. The unbleached kappa number of this pulp was 10.6.

Oxygen Delignification

The oxygen delignification experiments were performed in a laboratory high-shear mixer as described earlier [1]. A 110 g pulp sample was placed in a Hobart mixer and brought to a consistency of 11.0% for the control experiment (one chemical injected) and to 12.2% when surfactant (pitch dispersant) was used (2 chemicals injected). Each chemical being injected was brought to a volume of 100 mL in the chemical reservoirs. The pulp was then placed in the bowl of the high-intensity mixer and heated to the reaction temperature with pulse mixing (400 rpm) for 4 s every 30 s to avoid hot points. Once the pulp had reached 95°C, chemicals were injected in the following order: surfactant (when used) followed by NaOH. After the injection of chemicals (done at 800 rpm) the pulp was mixed at 1500 rpm for 4 s then pulse mixed at 400 rpm every 30 s for 4 s. The process conditions for the oxygen delignification reaction were: pulp consistency, 10.0%; retention time, 60 min; O₂ pressure, 0.41 MPa (60 psig); O₂ charge, 2.4%; and NaOH charge, 1.5% (oven-dry basis). No MgSO₄ was added to the stage.

At the end of the reaction, the pulp was drained with vacuum to 15 - 20% consistency and then diluted to approximately 1% consistency with deionized water, mixed for one min in a British Disintegrator and allowed to stand for 0.5 h. Afterwards, the pulp was drained through a 200-mesh screen with vacuum to a consistency of 15 - 20%. The pulp was diluted two more times to 1% consistency and drained (without disintegration).

Dispersants

The dispersants used in this work, Products A, B and C, are proprietary blends of LAEs and other...
surfactants. They were diluted with doubly distilled water to a concentration of 5% of the product, as received. For each run, the required amount of surfactant solution was pipetted into one of the injection reservoirs and deionized water was added to bring the solution volume to 100 ml. After each run, the reactor bowl and impeller were washed with water, followed by acetone, to avoid cross-contamination.

DCM Extraction
The extractions were conducted in a Tectator AB Soxtec System HT6 following a procedure published previously [5]. Prior to extraction, the pulp samples were ground using a Wiley mill and freeze-dried.

GC analysis of DCM extractives
The DCM extractives were methylated with diazomethane and analyzed using a Hewlett Packard 5890 Series II Plus gas chromatograph equipped with a DB5-HT capillary column, as described previously [1].

RESULTS AND DISCUSSION

Part A: Product comparison
In the first set of experiments, the deresination abilities of three blended products were compared at a charge of 2 kg/t to the oxygen delignification stage. Table I shows the resultant end pH values, kappa numbers, extents of delignification, pulp viscosities (selected experiments only) and DCM pulp extractives. It is clear that the end pH, kappa number, percent delignification and pulp viscosity were relatively unaffected by the dispersants, whereas there was a reduction of pulp extracts, especially with Product C.

The pre-oxygen delignification pulp for this work had a DCM extractives content of 0.36%, somewhat less than the 0.46% observed in previous work [1], likely because of less extractives in the aspen wood being pulped at the later time of sample collection. It is evident that an oxygen delignification stage and washing reduced the DCM extractives content in the pulp from 0.36 to 0.23%.

Part B: Product Dosage Response
We then proceeded to perform a dose-response evaluation of the most effective product from the selection tested, Product C. Figure 3 shows the results of the evaluation. It is evident that there is increased effectiveness as the dose increases. Moreover, the reduction at 2 kg/t was consistent with the results obtained in Fig. 2.

All three linear alcohol ethoxylate products gave some reduction in extractives. Product C had the most significant effect, reducing the extractives content by an additional 33%, for a total extractives reduction in the lab oxygen-delignification stage of almost 70%, Fig. 2.

It is interesting that the results are consistent with field experience with Product C. Typically, in a mill application, this product has shown a small to negligible effect at addition rates below a certain threshold value (which is dependent on system conditions, extractives content, etc.) but a significant effect at only slightly higher application rates. As a rule, this seems to reach a limit, where additional surfactant has little or no additional benefit. With the significant increase in extractives reduction between the 1 and 2 kg/t addition rates, Fig. 3, it is apparent that the upper threshold has not been reached. However, cost would normally prohibit the addition of more than 2 kg/t, unless extreme customer demands justify the application.

### TABLE I. Dispersant effectiveness comparison.

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>Control</th>
<th>Product A</th>
<th>Product B</th>
<th>Product C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersant charge, kg/t on pulp</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>End pH</td>
<td>12.4</td>
<td>12.4</td>
<td>12.4</td>
<td>12.3</td>
</tr>
<tr>
<td>Kappa number</td>
<td>7.5</td>
<td>7.5</td>
<td>7.6</td>
<td>7.6</td>
</tr>
<tr>
<td>Delignification, %</td>
<td>29.2</td>
<td>29.2</td>
<td>28.3</td>
<td>28.3</td>
</tr>
<tr>
<td>Viscosity, mPa.s</td>
<td>35.0</td>
<td>N.D.*</td>
<td>N.D.*</td>
<td>34.3</td>
</tr>
<tr>
<td>DCM extractives, %</td>
<td>0.23</td>
<td>0.21</td>
<td>0.21</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* Not determined
that Product C removes triglycerides and diglycerides (but not enhancing extractives reduction in oxygen delignification. more effective than the single component LAE surfactant at tion and washing. This blended surfactant product was much reduction relative to the initial pulp before oxygen delignifica-
over oxygen delignification alone, for a total of 69% extractives reduction, providing an additional 30% reduction blends, Product C showed superior performance in enhancing From the small group of selected linear alcohol ethoxylate
CONCLUSIONS
To better understand the action of the blended surfactant, Product C, the residual extractives on the fibers were chemically analyzed by gas chromatography. The results are shown in Fig. 4, where the main classes of chemical components in the extractives are plotted as a function of the charge of Product C. The left-hand set of data points gives the analysis of pulp extractives before oxygen delignification. The data at zero charge are, of course, for the blank experiment, in the absence of dispersant.
It is clear that, with increasing concentration of Product C, the concentrations of triglycerides, diglycerides, and sterols decreased with increasing charge of the dispersant. In previous work with a single LAE, we observed a decrease in triglycerides, but no change in diglyceride and sterol content. It would therefore appear that the advantage of the surfactant blend (Product C) is its ability to aid in the removal not only of triglycerides but also of diglycerides and sterols, hence delivering a remarkably superior deresination.

PRACTICAL IMPLICATIONS
We have discovered that a certain blend of LAE surfactants can be particularly effective for deresination during oxygen delignification. The next phase of this work will be its application in a mill trial.

ACKNOWLEDGEMENTS
To Francine Lafortune for the GC analyses; to Alain Gagné for plotting up the GC analyses of extractives; to Christine Lapointe for technical advice; and to Barbara van Lierop for initial review of the manuscript with helpful suggestions.

LITERATURE:

Résumé: Dans le procédé de mise en pâte kraft à partir de la fibre du peuplier, il a été démontré que le lavage au cours de l’étape de délignification à l’oxygène a un effet positif sur la réduction des matières extractibles dans la pâte. Nous avons déjà démontré que cet impact positif peut être amélioré par l’ajout, lors de la délignification à l’oxygène, d’un certain type générique de surfactant, soit le polyéthoxyéther d’alcools linéaire (LAE). À partir de ces résultats, d’autres travaux ont été effectués pour étudier les effets d’une sélection de mélanges de surfactants commerciaux, contenant des LAE visant à fournir une efficacité encore plus grande quant à la réduction des matières extractibles. L’une des préparations a été particulière-
ment efficace pour améliorer le retrait des matières extractibles à l’é-
tape de la délignification à l’oxygène.


Keywords: KRAFT PULPING, PUPULUS, WASHING, OXYGEN, DELIGNIFICATION, EXTRACTIVES, SURFACTANTS, MIXTURES, PITCH CONTROL, DISPERSANTS.